ALACHLOR MONITORING OF ONTARIO DRINKING WATER MAY -- NOVEMBER 1985

DECEMBER 1985

Ministry of the Environment

Ontario

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Minister

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EXECUTIVE SUMMARY

- Alachlor is a pre-emergent herbicide used widely in Southern Ontario in the cultivation of corn and soybeans. It has been used for the past 16 years and the amount used in Ontario in 1983 was 1.06×10^6 kilograms.

- It has been reported by Health & Welfare Canada that recent long-term animal feeding studies indicated alachlor caused tumors in some strains of rats and mice. Full registration of alachlor was cancelled by the Federal Minister of Agriculture and temporary registration given to it, which expires on December 31, 1985.

- Health and Welfare, Canada set an interim maximum acceptable concentration of 5 ug/L for drinking water.

- In 1984, alachlor was detected on five occasions (0.23 to 2.11 ug/L) in the treated water at five municipal waterworks (Dresden, Alvinston, Harrow, Mitchell Bay and Tilbury) and in some shallow private wells. Sixteen samples taken at Dresden from June to December indicated alachlor to be present in the untreated water six times (0.2 to 16 ug/L) and three times in treated water (0.3 to 7 ug/L).

- A monitoring program for municipal waterworks, private wells and ambient waters, together with a remedial action plan for sites where alachlor was detected in 1985 was prepared early in 1985 by the Ministries of Environment, Health, Labour, Agriculture & Food and representative Medical-Officers-of-Health.

- Treatment with powdered activated carbon (PAC) for the removal of alachlor at municipal waterworks was used at four waterworks (Dresden, Alvinston, Harrow and Mitchell Bay) where alachlor was detected in 1984.

- Sampling methods and analytical protocols were established together with the necessary quality assurance and quality control to ensure that the results of the survey were reliable.

- Total number of analyses for alachlor at municipal waterworks in 1985 was 1,719 (as of December 3). Alachlor was detected in untreated water at Dresden on six occasions (1.0 to 9.0 ug/L). It was never detected in the treated water, probably due to PAC treatment. Alachlor was not detected above 1.0 ug/L in untreated or treated water at any other waterworks monitored.

- Traces of alachlor (0.5 - <1.0 ug/L) were detected in the untreated water at 12 waterworks including Dresden for a total of 24 occasions. It was detected once at trace levels in the treated water at Paisley and Oneida.

- Additional analyses for pesticides and general chemistry were done for the municipal waterworks samples. Elevated nitrates and potassium levels tended to be present in untreated and treated water during or soon after rainfall events. Atrazine was detected at Dresden in the untreated water four times and at Cayuga once. Powdered activated carbon appeared to be effective in removing alachlor and atrazine when they were detected occasionally in the untreated water.

- Total number of analyses of private wells was 1,648 (as of December 3). Twenty one wells were contaminated with alachlor ($\geq$1.0 ug/L). Fifteen of these wells were used as a drinking source. Nine wells contained alachlor above 5.0 ug/L which necessitated the use of alternative water sources. Traces of alachlor were found in 22 other wells.

- Most alachlor contaminated wells were shallow and many were poorly constructed. However, some better constructed wells that were not shallow showed positive results for alachlor.

- Of the positive well sites, 12 appeared to be contaminated by overland surface runoff from treated fields and eight by contaminated ground water. One location appeared to be contamination from both sources.

- Additional pesticide and general chemistry analyses were done at well sites that had positive or trace contamination of alachlor. The information from these analyses illustrates the susceptibility of shallow, poorly constructed and maintained wells to contamination in general.

- Careless mixing operations of pesticides and disposal of containers was another source of contamination of surface and ground water, particularly shallow wells.

- Twelve beach and tributary stream sites were sampled once a week for 16 weeks until the end of August. One tributary stream was positive for alachlor on nine occasions. Two other tributary streams contained alachlor on three and one occasions. Samples from the Thames River were positive on two occasions.

- Samples of corn, soybeans and animal tissue from farms where alachlor was used or was detected in well water were analysed for alachlor. No alachlor was detected at or above the detection limit of 0.01 mg/Kg (0.01 ppm) dry weight.

- The alachlor monitoring program placed a heavy burden on OMAF and MOE laboratory staff and facilities and MOE field staff. Each alachlor analysis costs approximately $45 and the total program about $500,000 exclusive of senior administrative and co-ordinating staff time.

- An outside review of the program was conducted and it indicated that the monitoring program and analytical results were sufficiently accurate to indicate alachlor was present in drinking water supplies.

- Four individual home water treatment units were evaluated for removal of alachlor. Because of their generally limited capacity they are of little value where drinking as well as bathing and live-stock water is required to be treated.

- The alachlor monitoring program done in 1985 indicated alachlor was present at Dresden in untreated water on six occasions. It also indicated that traces of alachlor (0.5 - <1.0 ug/L) were present in untreated water at 12 locations including Dresden for a total of 24 occasions. Twenty one wells, 15 of which were used for drinking contained alachlor. Traces of alachlor were found in 22 other wells. Concentrations found in private wells were often in excess of the interim maximum acceptable concentration of 5 ug/L. This experience supports the need for a thorough knowledge of a pesticides toxicity, effect on health and its fate in the environment before it is registered for use.

CONCLUSIONS

1) Even though alachlor is biodegradable with a relatively short half-life in soil (3 weeks depending on soil type and climatic conditions) it was detected and quantified in some sources of municipal drinking water located in water sheds where alachlor was used.

2) Alachlor was detected in sources of municipal drinking water soon after rainfall and in highest concentrations shortly after its application to cropland.

3) Powdered activated carbon appears to be effective in removing alachlor from municipal drinking water.

4) Positive and trace quantities of alachlor reported in private wells tended to be associated with relatively shallow bored or dug wells located on properties where alachlor had been either mixed or used on adjacent land.

5) Shallow wells in sandy aquifers with a low organic content located in areas where alachlor was used were susceptible to contamination.

6) Poorly constructed and maintained wells were also susceptible to contamination.

7) Careless alachlor mixing operations and careless disposal of containers appeared to be a significant cause of contamination of farm wells.

8) Of the 21 positive well sites, 12 appeared to be contaminated by overland surface runoff from treated fields or spills and eight from contaminated ground water. One well appeared to be contamination from both sources.

9) Drained farmland on which alachlor is used will contribute significantly high concentrations of alachlor to main drainage ditches and in some cases to receiving streams.

10) Rainfall appeared not to cause rapid fluctuations in alachlor concentration in well waters except where direct run-off was entering a well or the soil in which the well was located was sandy with a low organic content.

11) No definite conclusions regarding the alachlor content of foodstuffs produced on farms where wells were contaminated or alachlor was used can be made except to note that samples of corn, beans, porcine tissue, hen eggs and one sample of human milk obtained on these farms did not contain alachlor at the detection limit of 0.01 mg/Kg (0.01 ppm).

12) The reporting level of 1.0 ug/L suggested at the beginning of the 1985 program was supported by the interlaboratory split-sample comparison for alachlor. The comparison indicated considerable agreement between the participating laboratories in the identification, recovery and quantification of alachlor at even low levels (above 0.1 ug/L).

13) Home treatment units, because of their generally limited capacity, are of little value where drinking as well as bathing and live-stock water is required to be treated.

14) The alachlor monitoring program placed a heavy burden on OMAF & MOE laboratories staff and facilities. Each analysis cost about $45 and the total program cost approximately $500,000 exclusive of senior administrative and co-ordinating staff time.

15) The alachlor monitoring program in 1985 which showed the herbicides presence in untreated water at one municipal location and traces of it in untreated water at 12 locations in total and its presence in 21 private wells,15 of which were used for drinking water sources along with the 22 wells which had trace concentrations indicates the need for a thorough knowledge of a pesticides toxicity, effect on health and its fate in the environment before it is registered for use.

1. INTRODUCTION

Alachlor, trade name Lasso, is a herbicide widely used in Southern Ontario (1,061 tonnes, 1983) to control weeds at the pre-emergent stage in the cultivation of corn and soybeans (properties in Appendix A). Because alachlor has been reported relatively recently to have caused tumors in animal studies (CD-1 strain female mice, Long-Evans strain rats*), its fate in the environment has become a concern. The Federal Department of Agriculture in co-operation with The Ontario Ministry of the Environment took water samples in 1984 at selected municipal waterworks and private wells in Southwestern Ontario and alachlor was detected at some of these sampling locations. Alachlor was given the status of temporary registration by the Federal Department of Agriculture for the 1985 season.

In 1985 The Ministry of the Environment (MOE) in co-operation with the Provincial Ministries of Labour, Health, Agriculture & Food, and with the assistance of the Federal Department of Agriculture drew up a sampling and analyses program for alachlor in municipal waterworks, private wells and beaches and tributary streams. An interim limit for alachlor in drinking water of 5 ug/L was recommended by Health & Welfare Canada.

This report provides details of the program and the analytical results.

* Alachlor Position Document I - EPA, U.S.A. Dec., 1984.

2. SAMPLING

Site Selection

Municipal waterworks, private wells and beaches and tributary streams were sampled specifically for alachlor. In addition pesticide scans were done weekly at Dresden, Paisley, Harrow and Cayuga until the end of August and continued at Harrow and Dresden until completion of the program. Other sites (5) were sampled monthly for pesticide scans as part of a regular sampling program.

Municipal Waterworks

Municipal sampling sites were selected on the following basis:

- Priority 1 sites were those where alachlor was detected in 1984, and where the source of water was from a stream draining an agricultural area subject to moderate to severe erosion or where the intake, if into a lake, was likely to be influenced by a similar drainage area.

- Priority 2 sites were surface and shallow well or spring supplies more remote from the point of application of alachlor than priority 1 sites, and/or influenced by drainage from a watershed with minor to moderate erosion.

- Priority 3 sites were generally locations remote from the influence of streams draining an agricultural watershed with intakes generally greater than 1,000 feet from shore, or deep wells protected by an aquiclude.

Private Wells

Private well sampling sites were selected on the following basis:

(a) In areas where positive results were obtained in 1984.

(b) In areas where corn and soybeans were being grown.

(c) Shallow wells generally less than 25 feet deep, e.g. sand points, springs susceptible to contamination.

(d) In sandy and gravelly areas or where physiography indicated possible susceptibility to contamination.

Private wells were selected finally using a grid system to provide as even a coverage as possible and to allow judgment in more intensive sampling. Additional sites were sampled on request if they met the conditions of (a), (b), (c) or (d).

Ambient Waters

Beaches and tributary stream sampling sites were selected on the following basis:

(a) In areas where positive results were obtained previously.

(b) In areas where corn and soybeans were being grown and drained farmland and/or agricultural runoff was likely to contribute to the tributary streams.

Sampling Method

(a) Grab samples were taken in one-litre amber or clear glass bottles with teflon or aluminum foil-lined caps. Amber bottles pre-cleaned at the MOE laboratory and shipped to the user were preferred. However, tests did show that the analyses was not compromised by use of clear glass bottles (Appendices B and D).

(b) A protocol for submission of samples was developed and appropriate submission forms provided to ensure quick tracing of sampling and minimal chance of sample loss or mix-up (Appendix C).

(c) Samples were submitted as soon as possible and storage when necessary was done with reasonable precautions against exposure to extremes of temperature and light etc. (Appendix D).

Municipal Waterworks

The need for representative samples was stressed and the grab samples of untreated and treated water were matched on the basis of plant retention time.

Private Wells

The sample was normally taken from a tap used to deliver drinking water after the tap had been allowed to run for one to three minutes.

Samples from wells with no convenient sampling taps were taken by lowering the sample bottle in a bucket and allowing the bottle to fill with a minimum of disturbance.

Samples that were found to be not representative of the water in the well were not included in this report.

Ambient Waters

Samples were taken and submitted as above.

Sampling Frequency

Frequency of sampling for municipal waterworks was based on the likely susceptibility of locations to alachlor contamination and was designated as follows:

Municipal Waterworks

Priority 1

- o 2 samples per week; raw and treated water; treated analysed only if detected in raw.*
- o event sampling daily following rainstorm for up to 5 days.

Priority 2

- o 1 sample per week; raw and treated water; treated analysed only if detected in raw.
- o event sampling as in Priority 1.

Priority 3

- o 1 sample per week; raw water only; if results positive, move up in priority.
- o event sampling - twice per week after rainstorm.
- o Some low susceptibility sites in Southwestern Ontario were sampled once per month.

It should be noted that the frequency of sampling above represents an optimal condition; conflicting manpower requirements and other factors influenced the actual frequency.

* NOTE: Both raw and treated water from Dresden, Alvinston, Harrow, Tilbury and Mitchell Bay were shipped and anlaysed.

Private Wells

o Private wells were usually sampled weekly, although the frequency was dictated by the range of positive results obtained.

Ambient Waters

o Beach and tributory stream locations were sampled weekly.

3. ANALYTICAL METHODS

The regular samples were analysed by two laboratories. The MOE lab at Rexdale analysed the municipal and a few ambient samples, while the Ontario Ministry of Agriculture and Food (OMAF) lab at Guelph analysed the samples from private wells and most ambient waters.

MINISTRY OF ENVIRONMENT

This methodology (details in Appendix D) was developed to provide a high sample throughput as well as a fast sample turnaround. Analytical results were required 30 hours after arrival of samples in the lab. A second methodology is available for alachlor as one component of the triazine analysis.

Extraction & Analysis:

The sample was solvent extracted, water was removed from the extract and it was concentrated. The concentrated extract was examined by gas chromatography using a nitrogen-phosphorus detector and external standard quantitation procedure, based on peak areas.

The dual column gas chromatographic method provided a high level of assurance of the correct identification of the compound.

All positive results were confirmed by mass spectrometry.

Quality Control and Quality Assurance:

Each set of samples was accompanied by a blank, a spike and a glassware rinse. Tap water was used as a blank and it was treated exactly as if it were a sample. This glassware/reagent blank monitored the quality of the procedure and reagents used. Details are in Appendix D.

Data Interpretation:

At the start of this program, a reporting level of 1.0 ug/L was established. To determine the confidence limits of the method at this level, a set of spikes at 1.0 ug/L in tap water was analysed and the standard deviation calculated.

Standard deviation: s = 0.1 ug/L.

According to the American Chemical Society (ACS), the detection limit was 10s or 1.0 ug/L. This indicated that a sample containing 1.0 ug/L would give a result of 1.0 $\pm$ 0.2 ug/L, 95 percent of the time. Values between 0.5 and 1.0 ug/L were reported as traces and values greater than 1.0 ug/L were reported to the nearest 0.1 ug/L. As the program progressed, it was thought that the detection limit should be substantiated.

A set of replicates at 0.5 ug/L was analysed and the standard deviation, s, was recalculated. In this case, s was equal to 0.05 ug/L; therefore, the method detection limit for the remainder of the program was 0.5 ug/L. However, to maintain consistency, values between 0.5 and 1.0 ug/L were still reported as traces, whilst values >1.0 ug/L were reported to the nearest 0.1 ug/L.

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Water samples were held in refrigerated storage at 5°C prior to extraction. Storage time for most samples did not exceed 24 hr. while the majority of samples which arrived on Friday were not extracted until the following Monday.

Extraction:

Water (1.0 L) was transferred to a separatory funnel and the pH was adjusted to 9 by addition of a few drops of dilute ammonium hydroxide. The water was shaken vigorously for 1 min. with 100 ml chloroform, the phases were allowed to separate, and the chloroform was drained through a plug of chloroform-prewashed and dried cotton and collected in a boiling flask. The extraction was repeated by shaking a second time for 1 min. with 100 ml chloroform. The combined extracts were evaporated to near dryness with rotary evaporation at 50°C, 10 ml iso-octane was added and evaporation to dryness was continued. The residue was dissolved in 5.00 ml methanol and transferred to a sample vial and sealed.

GLC Determination:

Analysis was carried out by capillary column gas chromatography with thermionic nitrogen-phosphorus specific detection operated under the following parameters:

Column - 15m x 0.25 mm i.d. and 0.25 um SPB-5 Supelco stationary phase.

Carrier gas - He at 2ml/min

Temperature - programmed from an initial temperature of 60°C at 20°C/min to 150°C followed by a 5°C/min rate to 250°C.

Under these conditions, alachlor elution time was 10.7 min. Quantitations were based on comparison of peak heights with reference standards and were made by an integrator/plotter.

Confirmation:

Samples which showed positive alachlor by capillary column chromatography were confirmed by re-analysis using gas chromatography with conductivity detection operated in the halogen-specific mode and a 1.8m x 2mm i.d. column packed with 5% Dexil 300 on 80/100 mesh Chromosorb W-HP and operated isothermally at 200^{o}C with helium carrier at 50 ml/min.

Recoveries:

Tap water was fortified with alachlor at concentrations of 1, 10, and 100 ug/L and carried through the analytical procedure as described above. Recoveries ranged from 85 to 95%. Final quantitative results are not corrected for recovery.

Quality Assurance:

Fortified and blank samples were run concurrently with every 10-15 samples at the beginning of the program and as the program progressed, QA/QC samples were gradually reduced to 1-2 weekly. Confirmation of positive samples were conducted as described above using alternate column and alternate detector GLC while during the initial stages of the program, all positives were confirmed by GC/MS using alachlor and deuterated alachlor as references.

INTERLABORATORY SPLIT-SAMPLE COMPARISON FOR ALACHLOR

The ability of different laboratories to obtain similar measurements on the same sample is an important agreement between the standards used for method calibration, similar ability to recover the test constituent from the sample matrix and a similar ability to carry out the test procedure. The results of such a study of interlaboratory agreement in measuring alachlor are reported below.

Dresden Raw Water Samples

Throughout the alachlor study, Dresden raw water samples were collected in 4.5 liter containers using the routine sampling procedure, for use in a split-sample interlaboratory comparison program. These were submitted to the MOE laboratory where they were carefully split into 1 liter portions and forwarded to the pesticides laboratories of MOE (Rexdale), OMAF (Guelph), and Heidelberg College (HC) (Tiffin, Ohio) for routine alachlor analysis. Thirty-two samples were split as of August 30, 1985.

The validity of analytical measurement depends on proper identification of the constituents which have responded to the test method used. It is accepted practice that a result is reported only if it can be confirmed under different analytical conditions, for example, two different GC columns or different detectors. Otherwise the compound is reported as not detected. Confirmation by GC/MS is preferred if possible. Even under these conditions, it is possible that other constituents may interfere with the quantitation of alachlor. Therefore, when different methods are employed, comparability in results implies an added level of data reliability and accuracy. The instrumental conditions employed by the participating labs are tabulated in Appendix E.

The agreed MOE reporting protocol for the alachlor study was to report not detected (N.D.) if the measured result was below 1 ug/L. At the low levels being discussed here, the area of the peak being easured is extremely dependent on the points on the baseline at which the area counting is started and ended. Incomplete separation

of peaks and noisy or drifting baselines can affect the repeatability and accuracy of the quantification process. Adsorption, contamination, or other chemical and physical processes may affect the analytical recovery of the method during sample extraction and cleanup stages. Studies of reproductibility and recovery at MOE indicated that results above 0.5 ug/L were increasingly reliable.

When the split-sample results were reported it was realized that a statistical evaluation of interlaboratory agreement would not be possible, because the majority of results were reported to be below 1 ug/L.

In order to evaluate the comparability of data between laboratories, the analysts were then asked to report the measured value even if it was below 1 ug/L. Table 1 gives these values to the nearest 0.01 ug/L whenever both channels detected a peak at the alachlor retention time. The concentration of alachlor in each sample was taken as the lowest of the two values. The MOE data was calculated based on the response of a nearby standard in the run. Note that the second decimal place is not considered significant.

The following observations suggest that there was considerable agreement between these laboratories at the first decimal place, even below 1 ug/L. The fact that chromatographic conditions varied widely from channel to channel serves to support the premise that all labs were confirming the presence of alachlor.

a) MOE reported 27 samples were less than 1 ug/L. This was confirmed by the other two labs.

b) All three labs agreed that 23 samples were below 0.3 ug/L.

c) Two samples (OW29-0239 and OW29-0296) measured about 0.4 to 0.7 ug/L by all labs.

d) MOE measured 1.26 ug/L on sample OW29-0143 but reported interference. The other labs measured about 0.5 ug/L.

Table 1

Split-sample comparison data for alachlor

Sample #	MOE		OMAF	HC	
Channel	1	2	1	1	2
OW19-0021	N.D.		N.D.	N.D.	
OW19-0110	N.D.		N.D.	N.D.	
OW19-0166	N.D.		N.D.	N.D.	
OW20-0232	N.D.		N.D.	N.D.	
OW21-0094	N.D.		N.D.	0.17	0.28
OW21-0170	N.D.		N.D.	N.D.	
OW22-0048	N.D.		N.D.	N.D.	
OW22-0310	N.D.		0.20	N.D.	
OW23-0106	2.65	2.56	2.6	1.88	1.91
OW23-0335	N.D.		0.28	N.D.	
OW24-0032	N.D.		0.37	N.D.	
OW24-0169	N.D.		N.D.	0.06	
OW25-0048	N.D.		N.D.	Broken	
OW25-0299	1.36	1.93	1.1	0.96	0.97
OW26-0407	N.D.		N.D.	0.10	0.25
OW28-0021	N.D.		N.D.	N.D.	
OW28-0073	N.D.		N.D.	N.D.	
OW28-0247	N.D.		N.D.	N.D.	
OW29-0080	0.07	0.26	N.D.	N.D.	
OW29-0143	intf	1.26	0.57	0.38	0.53
OW29-0239	0.52	0.21	0.50	0.45	0.48
OW29-0296	0.70	0.66	0.54	0.43	0.57
OW30-0020	1.02	1.12	0.85	0.80	0.99
OW30-0064	1.17	1.04	0.54	N.D.	
OW30-0174	0.26	0.24	N.D.	N.D.	
OW31-0068	0.26	0.19	N.D.	N.D.	
OW31-0271	0.10	0.07	N.D.	N.D.	
OW32-0067	0.11	0.05	N.D.	N.D.	
OW33-0109	N.D.		N.D.	N.D.	
OW34-0052	0.13	0.05	N.D.	N.D.	
OW34-0187	N.D.		N.D.	N.D.	
OW35-0075	N.D.		N.D.	N.D.	

NOTE: In this table N.D. means that no peak (<0.1 ug/L) was observed or that it was not found in both channels used for confirming alachlor identity.

This data is reported here for QA purposes only. The project lower reporting limit was 1 ug/L.

e) Three samples (OW25-0299, OW30-0020, OW30-0064) were measured between 1.0 and 1.4 ug/L by MOE. The other labs tended to reported somewhat lower values within the range N.D. to 1.1 ug/L.

f) One sample (OW23-0106) was reported by MOE and OMAF to be 2.6 ug/L whereas HC reported 1.9 ug/L.

Technically, this data is very close to the analytical limit of detection. The level of agreement between labs is surprisingly good. In order to determine whether a bias exists between these laboratories would require much more data.

Spiked Tap Water

In order to evaluate the recovery achieved by these labs, three samples of Toronto tap water were spiked with known amounts of alachlor and split between the above three laboratories and the Agriculture Canada Pesticides lab in Ottawa. The unspiked tap water measured less than 0.1 ug/L. Results indicated a general under-recovery of between 50% and 90% of the expected value, but the accuracy of these extremely low spike solutions is not known. The results were:

Sample #	Design	MOE	OMAF	HC	AG.CAN
May 14	2.0*	1.2	1.0	1.15	-
Aug 09 a)	1.0*	0.85	0.86	0.85	1.08
b)	5.0*	4.5	4.5	2.9, 3.5	3.54

* the accuracy of these values is not verifiable but the recoveries are about as expected

Conclusion

This data demonstrates considerable agreement between the participating laboratories in the identification, recovery and quantification of alachlor at very low levels. Table 1 indicates that alachlor was probably being detected reliably in several of these samples at levels above 0.1 ug/L. At the same time it indicates the uncertainty attached to data produced at the low limits of measurement. The agreement between laboratories was better than anticipated based on the known performance of the individual analytical system. This data lends support to reporting to the nearest 0.1 ug/L, even below 1 ug/L, in future studies.

4. RESULTS OF SURVEY

Sampling of municipal water plants started on May 2, private well sampling started on May 24 and beach and stream locations were first sampled on May 14. Sample locations are listed in Tables 2, 3 and 4 respectively.

Municipal Waterworks

Forty-four municipal waterworks and five Indian reserve waterworks were monitored for a total of 1,719 samples analysed, 1,412 from the raw water and 301 from the treated water as of December 3 (Table 2). Most of these raw and treated samples were from the Southwestern Region (1,254), while other regions sampled had from 119 to 192 samples analysed.* The number was higher in the Southwestern Region because alachlor was detected in the water in 1984 and more alachlor is used in this area. Thirty five waterworks were sampled in this region with an average of 28 raw samples per treatment plant and a maximum of 84 samples of the Dresden raw water.

Of all the municipal waterworks sampled alachlor was only detected (at or above 1.0 ug/L) in the Dresden raw water, where it was found on six occasions at concentrations ranging from 1.0 to 9.0 ug/L (Table 5). These positive results tended to occur soon after rainfall. Trace results (0.5 to less than 1.0 ug/L) were found in the Dresden raw water on seven occasions and they also tended to occur after rainfall. Turbidity, total nitrates and potassium in the untreated water tended to increase at the time alachlor was detected (Table 5) and this would be consistent with runoff from agricultural fields.

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* See Map, Appendix G, for MOE regions and Ontario counties.

Table 2

MUNICIPAL WATERWORKS SAMPLING LOCATIONS

West Central Region

County	Municipality	Source	Raw		Treated	
			No. Samples	No. Positive	No. Samples	No. Positive
Brant	Brantford	Grand River	39	0	2	0
Dufferin	Shelburne	Well 4	10	0	0	0
	Shelburne	Well 5	11	0	0	0
Haldimand	Cayuga	Grand River	38	0	2	0
	Dunnville	Grand River	12	0	0	0
	Simcoe	Wells	15	0	0	0
Norfolk	Delhi	North Creek	38	0	2	0
	Port Rowan	Lake Erie	22	0	1	0
TOTALS			185	0	7	0

As of Dec. 3, 1985

Table 2 (continued)

MUNICIPAL WATERWORKS SAMPLING LOCATIONS

Southwestern Region

County	Municipality	Source	Raw No. Samples	Raw No. Positive	Treated No. Samples	Treated No. Positive
Bruce	Hanover	Ruhl Lake	23	0	0	0
	Paisley	Saugeen River	36	0	2	0
Elgin	Elgin W.S.S.	Lake Erie	29	0	2	0
	Port Stanley	Lake Erie	44	0	0	0
Essex	Amherstburg	Detroit River	49	0	1	0
	Belle River	Lake St. Clair	32	0	1	0
	Harrow	Lake Erie	69	0	49	0
	Stoney Point	Lake St. Clair	52	0	2	0
	Union W.S.S.	Lake Erie	30	0	0	0
	Windsor	Detroit River	37	0	1	0
Huron	Baldwin Subdivision	Lake Huron	29	0	0	0
	Centralia/Huron Park	Wells	30	0	0	0
	Hensall	Wells	2	0	0	0
	Lake Huron W.S.S.	Lake Huron	6	0	0	0
Kent	Blenheim	Lake Erie	28	0	0	0
	Dresden	Sydenham River	84	6	65	0
	Mitchell Bay	Lake St. Clair	73	0	51	0
	Thamesville	Wells	4	0	0	0
	Tilbury	Lake St. Clair	47	0	33	0
	Wallaceburg	Chanal Ecarte	43	0	6	0

Table 2 (continued)

County	Municipality	Source	Raw		Treated	
			No. Samples	No. Positive	No. Samples	No. Positive
Lambton	Alvinston	Sydenham River	57	0	44	0
	Bright's Grove	Lake Huron	3	0	0	0
	Kettle Point Reserve	Lake Huron	1	0	0	0
	Walpole Island Reserve	Lake St. Clair	30	0	0	0
Middlesex	Caradoc Reserve	Thames River	21	0	0	0
	Deleware	Wells	3	0	0	0
	Dorchester	Wells	1	0	0	0
	Komoka Springs	Wells	3	0	0	0
	Moravian Reserve	Thames River	27	0	0	0
	Mount Brydges	Wells	18	0	0	0
	Oneida Reserve	Thames River	23	0	0	0
	Strathroy	Wells	25	0	0	0
Oxford	Thamesford	Wells	2	0	0	0
	Woodstock	Wells	28	0	0	0
Perth	Mitchell	Wells	2	0	0	0
TOTALS			991	6	257	0

As of Dec. 3, 1985

Table 2 (continued)

MUNICIPAL WATERWORKS SAMPLING LOCATIONS

Southeastern Region

County	Municipality	Source	Raw		Treated	
			No. Samples	No. Positive	No. Samples	No. Positive
Hastings	Frankford	Well #1	12	0	0	0
		Well #2	4	0	0	0
	Trenton/Mayhew Creek	Wells	13	0	1	0
	Trenton/Murray Well	Well	2	0	2	0
Prescott	Casselman	South Nation River	32	0	4	0
	Plantagenet	South Nation River	43	0	5	0
Stormont, Dundas & Glengarry	Alexandria	Alexander Lake	30	0	6	0
TOTALS			136	0	18	0

As of Dec. 3, 1985

Table 2 (continued)

MUNICIPAL WATERWORKS SAMPLING LOCATIONS

Central Region

County	Municipality	Source	Raw		Treated	
			No. Samples	No. Positive	No. Samples	No. Positive
Simcoe	Brechin	Lake Simcoe	62	0	10	0
Victoria	Lindsay	Scugog River	38	0	9	0
TOTALS			100	0	19	0

As of Dec. 3, 1985

Table 3

PRIVATE WELLS

West Central Region

County	No. Wells Sampled	No. Positive Wells	Total No. Samples	No. Positive Samples
Brant	3	0	22	0
Haldimand-Norfolk	10	0	54	0
Waterloo	3	0	36	0
TOTALS	16	0	112	0

As of Dec. 3, 1985

Table 3 (continued)

PRIVATE WELLS

Southwestern Region

County	No. Wells Sampled	No. Positive Wells	Total No. Samples	No. Positive Samples
Bruce	2	0	9	0
Elgin	25	0	63	0
Huron	11	1	42	4
Kent	27	3	204	5
Lambton	53	2	242	10
Essex	7	1	48	5
Middlesex	71	8	354	28
Oxford	4	0	4	0
Perth	1	0	3	0
TOTALS	201	15	969	52

As of Dec. 3, 1985

Table 3 (continued)

PRIVATE WELLS

Southeastern Region

County	No. Wells Sampled	No. Positive Wells	Total No. Samples	No. Positive Samples
Russel	18	0	65	0
Stormont, Dundas & Glengarry	4	1	6	1
Prince Edward	22	2	102	2
Frontenac	1	0	1	0
TOTALS	45	3	174	3

As of Dec. 3, 1985

Table 3 (continued)

PRIVATE WELLS

Northeastern Region

County	No. Wells Sampled	No. Positive Wells	Total No. Samples	No. Positive Samples
Manitoulin	5	0	8	0
TOTALS	5	0	8	0

As of Dec. 3, 1985

Table 3 (continued)

PRIVATE WELLS

Central Region

County	No. Wells Sampled	No. Positive Wells	Total No. Samples	No. Positive Samples
Durham	2	0	2	0
Northumberland	10	1	110	1
Victoria	6	1	86	1
Peterborough	4	0	38	0
Simcoe	14	1	147	16
York	2	0	2	0
TOTALS	38	3	385	18

As of Dec. 3, 1985

Table 4

AMBIENT WATER SAMPLE LOCATIONS

Central Region

County	Ambient/Beach Site	Source	No. Samples	No. Positive
Peterborough	Dunschede Pond	Farm Pond	1	0
Simcoe	Perkins Pond	Farm Pond	1	0
	Kneeshaw Pond	Farm Pond	1	0
TOTALS			3	0

As of Dec. 3, 1985

Table 4 (continued)

AMBIENT WATER SAMPLE LOCATIONS

Northeastern Region

County	Ambient/Beach Site	Source	No. Samples	No. Positive
Manitoulin	McKenzie Pond	Farm Pond	1	0
TOTALS			1	0

As of Dec. 3, 1985

Table 4 (continued)

AMBIENT WATER SAMPLE LOCATIONS

Southeastern Region

County	Ambient/Beach Site	Source	No. Samples	No. Positive
Prince Edward	SE-85-6A	Pond	1	0
TOTALS			1	0

As of Dec. 3, 1985

Table 4 (continued)

AMBIENT WATER SAMPLE LOCATIONS

Southwestern Region

County	Ambient/Beach Site	Source	No. Samples	No. Positive
Grey OR Bruce	Saugeen River	Saugeen River	9	0
Elgin	Port Stanley - Inlet Stream	Tributary of Lake Erie	16	0
	Port Stanley - Beach	Lake Erie	16	0
Kent	Rondeau Bay - Inlet Stream	Tributary of Lake Erie	27	9
	Rondeau Bay - Beach	Lake Erie	16	0
	Thames River	Thames River	11	2
Lambton	Mud Creek	Tributary of Lake Huron	4	0
	Peters Pond	Farm Pond	1	0
	Downie Pond	Farm Pond	1	0
Middlesex	Rommele Property	Farm Pond	2	2
	Cold Stream - Inlet Stream	Thames River	16	0
	Cold Stream Park - Beach	Thames River	16	0
	Fanshaw Lake - Inlet Stream	Thames River	16	0
	Fanshaw Lake - Beach	Thames River	16	0
Oxford	Pittock Lake - Inlet Stream	Thames River	16	3
	Pittock Lake - Beach	Thames River	16	0
Perth	Wildwood Lake - Inlet Stream	Thames River	16	1
	Wildwood Lake - Beach	Thames River	15	0
	Pond Water		1	0
TOTALS			231	17

As of Dec. 3, 1985

Table 4 (continued)

AMBIENT WATER SAMPLE LOCATIONS

West Central Region

County	Ambient/Beach Site	Source	No. Samples	No. Positive
Brant	Pletzer Pond	Farm Pond	9	0
Brant OR Haldimand	Grand River	Grand River	21	0
TOTALS			30	0

As of Dec. 3, 1985

TABLE 5

DRESDEN ALACHLOR & GENERAL CHEM-PESTICIDES

Untreated Water

Date		Alachlor Conc ug/L	Turbidity FTU	Nitrate As N mg/L	Potassium As K mg/L	Remarks
May	28	ND	35	2.1	2.6	
"	30	ND	49	2.1	1.6	May 30-31 rain event
"	31	TRACE				
June	1	9.0				June 1-3 rain event
"	2	3.2				
"	3	2.2 (3.0 OMAF)	51	7.6	3.2	
"	6	ND	43	3.0	2.6	Insuff. samples for pesticides
"	10	ND	55	1.97	2.9	
"	11	TRACE (OMAF)				
"	13	ND	43	1.9	2.8	All pesticides < MDL* insuff. for triazines
"	17	ND				
"	18	ND	54	2.6	2.85	
"	19	2.1	72	12.5	3.8	
"	20	1.4	53	10.6	3.6	
"	21	ND	62	6.5	3.25	June 17-22 rain event
"	22	TRACE	47	5.8	3.05	
"	24	ND	52	5.8	3.15	
"	25	TRACE (OMAF)				
"	26	-	52	3.50		All pesticides <MDL
"	27	ND	44	3.0	2.75	
July	2	ND				
"	4	ND	12.8	3.20		All pesticides <MDL
"	8	ND				
"	9	ND				
"	10	-	18.10	2.8		All pesticides <MDL except atrazine 2.6 ug/L
"	11	ND	37	2.1	3.0	
"	15	ND	30	1.3	3.0	July 15-19 rain event
"	16	1.0	105	8.9	3.05	
"	17	TRACE	119	5.2	4.3	All pesticides <MDL
"	18	ND	125	11.2	4.65	
"	19	TRACE	101	13.8	5.3	
"	22	TRACE	80	8.6	3.3	
"	23	ND				July 24 all pest. <MDL except atrazine 2.0 ug/L metribuzin 2.35 ug/L
"	29	ND	58	3.2	3.8	July 31 all pest. <MDL except atrazine 2.2 ug/L
Aug.	1	ND	48	1.2	3.1	
"	6	ND	53	0.26	2.85	
"	12	ND	36	<0.01	2.85	
"	13	ND				Aug. 28 all pest. <MDL except atrazine 0.9 ug/L

* <MDL - less than minimum detection limits
ND = Not detected
\- No alachlor sample taken

The treated water at Dresden was consistently negative for alachlor, probably due to the addition of powdered activated carbon (PAC) in the water treatment process. This was initiated at several water plants where contamination seemed possible and is discussed in Section 5.

Trace quantities of alachlor were detected in the raw water at 11 other locations besides Dresden (Table 6). Five of these locations were in the Southwestern Region, four in the West Central Region and two in the Southeastern Region. The one trace level found in Windsor raw water was associated with the highest turbidity in the accompanying support analysis. Trace quantities were also found on one occasion in the treated water at the Oneida Indian reserve (no treatment provided) and Paisly (Table 6).

Pesticide scans (Appendix F) were done weekly at Dresden, Harrow, Cayuga and Paisley. The results at Dresden were below detection limits in the untreated water except for four occasions when atrazine was detected at 2.6, 2.0, 2.2 and 0.9 ug/L and one occasion when metribuzin was detected at 2.35 ug/L. The 2.0 ug/L atrazine and 2.35 ug/L metribuzin were obtained after rainfall had occurred (Table 5). No pesticides above detection limits were reported in the treated water at Dresden, possibly, because of the use of powdered activated carbon. At Cayuga, atrazine was detected on one sampling date (Sept. 5, 1985) in the raw and treated water at 1.7 and 1.5 ug/L respectively. No pesticides above detection limits were reported at the other two sites.

Pesticide scans were done on a monthly basis at nine locations (Alvinston, Amherstburg, Port Stanley, Stoney Point and Wallaceburg plus the four locations on weekly scans). No pesticides above the minimum detection limits were reported.

TABLE 6

WATERWORKS WHERE A TRACE* OF ALACHLOR WAS REPORTED

Location		Date	
Alexandria	(UNT)	June 20	
Alvinston	(UNT)	May 30	
"	"	June 20	
"	"	June 22	
Brantford	(UNT)	June 13	
Cayuga	(UNT)	May 30	
"	"	June 6	
Casselman	(UNT)	June 20	
Delhi	(UNT)	June 6	
Dresden	(UNT)	May 31	
"	"	June 11	
"	"	June 22	
"	"	June 25	
"	"	July 17	
"	"	July 19	
"	"	July 22	
Oneida	(UNT)	May 28	NOTE: Not a municipal waterworks, UNT & TRTD same
Paisley	(UNT)	May 30	NOTE: Duplicate Samples
"	"	June 1	
"	(TRTD)	May 30	
Port Rowan	(UNT)	June 13	
"	"	June 19	
Stoney Point	(UNT)	May 31	
" "	"	June 22	
Windsor	(UNT)	June 1	

(UNT) = Untreated
(TRTD) = Treated

* Trace concentration - a positive sample with a concentration less than 1 ug/L but greater than 0.5 ug/L.

Private Wells

Many of these locations were sampled once only (spot checks on request). Those considered susceptible to contamination and those where alachlor was detected were regularly sampled.

There were 1,648 water samples taken from 305 private wells up to December 3 (Table 3). There were 201 wells sampled in the Southwestern Region and from 5 to 45 in the other regions sampled. The number of wells in the Southwestern Region that contained alachlor was 15, while three were positive in the Central and Southeastern Regions and none in the Northeastern Region. Only single positive samples were found in the positive wells in the Southeastern Region. Details on the concentrations, possible route of contamination and action taken are summarized in Appendix H. In the Central Region, 16 positive samples were from one site while the rest were single positive samples. In the Southwestern Region alachlor was found in five counties, in from 4 to 14 percent of the wells sampled. More than one positive well was found in the counties of Kent, Lambton and Middlesex, with the latter having more than all the others combined. Almost one third of the samples (354) were taken from wells in Middlesex County, and those contained more than half of the positive samples (28) found in the region.

There were 21 positive wells and most were shallow dug wells, many being subject to probable surface water contamination. Almost half were located in sandy soil. Usually alachlor was mixed or was used on adjacent land. Fifteen of these wells were used for drinking water sources and five of these had concentrations over 5 ug/L, which necessitated the supply of uncontaminated water. Trace quantities of alachlor (0.5 - <1.0 ug/L) were reported at most wells where concentrations were found above 1 ug/L and an additional 22 wells. About one quarter of the wells with positive or trace results for alachlor from the Southwestern Region had elevated nitrate and/or potassium levels, indicating probable ground water contamination from fertilized fields. In Appendix H, conclusions are reached about the probable or possible source of the alachlor contamination in each of the positive wells. There were eight wells

where the alachlor appeared to enter the well via contaminated ground water and 12 wells where the source appeared to be due to overland surface runoff from treated fields or a spill of the chemical in the vicinity of the well. One location appeared to get contamination from both overland runoff and contaminated ground water.

Private wells where alachlor was found were usually sampled weekly. These samples were rarely continuously positive for alachlor; most had only a few positive samples in May, June or July and if sequentially positive often showing a peak near the end of May. This is shortly after the herbicide was applied and possibly due to limited surface water contamination of the well. Some wells had positive samples separated by several samples where alachlor was not detected. The reason for these sudden occurrences may have been related to alachlor being flushed from sandy soil by rainfall. Three wells had samples almost continuously positive for alachlor, showing gross contamination that was probably associated with a spill of the chemical or grossly contaminated ground water. Since adjacent wells were usually negative for alachlor, the aquifer or an adjacent aquifer were not contaminated.

When a well contained alachlor greater than 1 ug/L but less than 5 ug/L, a joint inspection by local health unit and Ministry of Environment staff was done. The owner was advised that the water was within the Health and Welfare Canada guideline of 5 ug/L. Immediate re-sampling and analysis of the well was done. If the result of this resample was higher than the original concentration, then non-use of the well for drinking was suggested with an alternate source of drinking water being offered by the Ministry of Environment. Testing of the well continued until it was established that no alachlor was present or its concentration had exceeded the guideline of 5 ug/L. If the concentration of alachlor in a well was equal to or greater than 5 ug/L a joint inspection was done, and the Medical-Officer-of-Health advised non-use of the well and an alternate supply of drinking was offered by the Ministry of the Environment.

Remedial action to clear contamination from the well was discussed with the user, and monitoring of the well continued on a weekly basis. Appendix H contains a list of the wells where alachlor was detected and the conditions at the well and action taken.

Ambient Waters

The majority of samples taken from ambient water for alachlor analysis were from the Southwestern Region where 231 samples were examined as of December 3. The other four regions sampled took a total of 45 samples and all were negative for alachlor (Table 4). In the Southwestern Region most of the analyses (196) were from paired samples of a stream and a beach in the same area. These paired samples were from the counties of Elgin, Lambton, Middlesex, Kent, Oxford and Perth. Positive stream samples were found in the latter three counties. All the samples taken from beaches were negative.

Most positive samples were from Rondeau Bay inlet stream, Kent County, where concentrations of 1.3 to 51.0 ug/L were found on nine occasions; four of the samples were over 30 ug/L and the rest were below 11 ug/L. The first samples collected on May 14 were positive as were most in the rest of May and June, while just one of weekly samples in each of July and August was positive. Streams into Pittock Lake, Oxford County, and into Wildwood Lake, Perth County, were positive in May and June with concentrations of 1.2, 1.5 and 1.6 ug/L at the first location and 2.0 ug/L at the second location.

Four other positive samples were found in the Thames River samples, Kent County (5.3 and 6.9 ug/L), and a farm pond in Middlesex County with concentrations of 15 and 12 ug/L. These samples were collected in May, June and July. There have been no positive ambient water samples since August 20.

Time Trend and Weather Pattern Trend

Surface Water

The variability of rainfall and its intensity differ sharply in relatively close areas. This makes it difficult to draw any conclusions other than that high pesticide concentrations in run-off are due to high soil-moisture content of soil during rain and following the application of alachlor in the spring and summer months. The concentration of alachlor in the run-off depends on the intensity and magnitude of rainfall and amount of alachlor present in the field.

Generally the total rainfall recorded at Dresden in May is about 57 mm. In May, during this study it was 75.8 mm with the majority occuring the last two weeks of May. The heaviest 24-hour rainfall of 21.7 mm occurred on May 30 (night), whilst 17 mm was recorded for May 27. It is notable that the concentrations of alachlor in the untreated water at Dresden on June 1, 2 & 3 were 9.0, 3.2 & 2.2 ug/L respectively.

Generally the total rainfall in the vicinity of Dresden in June is about 83 mm. In June during this study it was 66.5 mm. The heaviest 24 hour rainfall was 20.8 mm on June 11. For July the rainfall for the Dresden area is usually 63 mm; for July 1985 it was 66.4 mm which indicates a fairly normal month for total precipitation.

The Chatham area, which is close to Dresden, recorded 58.6 mm for June versus a normal June total precipitation of 77 mm. In July 107.2 mm of rain fell in contrast to the expected 77 mm. The heaviest rainfall, 68 mm, occurred on July 14 in the Chatham area whilst Windsor recorded only 15.4 mm on this day.

The data in Table 5 from the analyses of water samples of Dresden's untreated water show higher concentrations of alachlor during the first significant rainfall following spring planting. The finding of alachlor residues in the untreated water at Dresden in samplings

during rainfall in June and July indicates that alachlor persisted for more than a month.

Ground Water

Several factors influence the likelihood that an agricultural pesticide will leach below the unsaturated root zone to the saturated zone and eventually contaminate the ground water used for drinking water. The persistence and mobility of the pesticide are obviously key factors, as is the rate of decay in the soil environment. More rapidly decaying pesticides are less likely to leach than the more persistent. The potential to leach is also governed by a pesticide's solubility and its soil-binding property. The soil partition coefficient (Kd), the ratio of pesticide quantity adsorbed to soil to that quantity dissolved in water is a measure of a pesticide's soil-binding. Pesticides have a tendency to leach when the soil half-life is greater than 2-3 weeks; the solubility is greater than 30 ppb; and the Kd is less than 5. Soil half-life values for alachlor are about 3 weeks, its solubility 240 ppm and Kd values reportedly in the range of 0.6-8.1 depending on soil type, with most values around 4.0.

Soil incorporation of a pesticide tends to increase the leaching potential relative to surface or foliar application. Pesticides which biodegrade do so more slowly in cooler temperatures.

Alachlor contamination of ground water would appear to be generally confined to relatively shallow bored or dug wells in quite permeable soil. The route to wells may be through normal infiltration and surface run-off. The construction and maintenance of the well will influence the amount of contamination. Some of the highest levels of contamination occurred where careless mixing of the pesticide or disposal of the containers was the contributing factor. Rainfall would not tend to cause rapid fluctuations in alachlor concentration in well waters except where direct runoff was entering a well or the soil in which the well was located was sandy with a low organic content.

5. TREATMENT TECHNIQUES FOR REMOVAL OF ALACHLOR

MUNICIPAL WATERWORKS

Bench Studies

Because alachlor had been detected in the untreated and treated drinking water at some water treatment plants (5) in 1984 and because there was a likelihood that it would be used in the 1985 growing season, health concerns dictated that the Ministry of the Environment should evaluate practical methods of treatment to reduce the concentration of alachlor in drinking water. To do this, the Drinking Water Section of the Water Resources Branch did bench-scale treatability studies on alachlor-spiked untreated water from Dresden using alum with activated silica, granular activated carbon (before and after filtration) and powered activated carbon added to untreated water and to the supernatant after settling. The alachlor-spiked Dresden water was prepared in 19-litre batches to approximately 50 ug/L concentration of alachlor.

The results of the treatability studies were as follows:

(1) Conventional drinking water treatment and conventional treatment plus lime softening were not effective in the removal of alachlor spiked into Dresden water.

(2) Conventional treatment plus clay addition exhibited some alachlor removal but not enough to make the process a viable alternative.

(3) Conventional treatment plus activated carbon was effective in the removal of alachlor spiked into Dresden water.

Granular activated carbon (GAC) was most efficient with greater than 99% removal of alachlor when used after filtration.

Powdered activated carbon (PAC) added to the raw water prior to conventional treatment exhibited removals of 80 to 98% for dosages from 50 to 100 mg/L PAC. PAC added to the supernatant, simulating addition to the top of the clarifier, exhibited removals in the range of 90% for dosages ranging from 25-75 mg/L PAC.

Field Experiences

Powdered activated carbon was chosen as many water treatment plants do add it now intermittently for taste and odour control. Supplies of it were also readily available. To add it at the dosages needed (25-75 mg/L) on a permanent basis would require better storage and handling facilities than now available to prevent the fine material fouling the waterworks.

As with most bench-scale studies, there were some reservations about the effect of powdered activated carbon in actual practice. Its effect on the overall treatment process at Dresden and other sites where powdered activated carbon was to be used was not completely known. However, turbidity reduction and bacteriological quality has remained excellent throughout field addition of powdered activated carbon. Powdered activated carbon was very effective in that no alachlor was detected in the treated water at Dresden or at any other location where powdered activated carbon was used when alachlor or traces of it were reported in the untreated water.

Atrazine was also reduced to below detection limits in the treated water on the four occasions it was detected in untreated water at Dresden.

Private Water Systems - Home Treatment Devices

Four carbon type point-of-use water filters and one domestic size reverse osmosis unit were tested at Ontario Research Foundation to determine their ability to remove alachlor from drinking water. Three of the test units removed 75 percent or more of the alachlor over a priod of 15 days in an accelerated test during which

approximately 1,000 gallons was treated. A fourth test filter had variable removal ranging from 18 to 83 percent. The reverse osmosis unit removed about 80 percent of the alachlor under the conditions of testing. Individual units were severely limited because they were not large enough to be able to produce enough water for bathing or livestock watering.

6. COST

The costs of the Alachlor Program were as follows:

*PAC, *GAC, Coagulant Bench Studies	$16,000.00	$16,000.00
PAC Field Application (up to Sept. 30)		
Harrow	$21,486.00	
Tilbury	900.00	
Mitchell Bay	1,169.00	
Dresden	10,903.00	
Alvinston	3,773.00	
	38,231.00	
Carbon Containment	$30,000.00	
	$68,231.00	$68,231.00
Outside Consultants (5025 Aug. 31)		
ORF - Home Treatment Devices	$14,824.00	
Dillon - Independent Review of Program	$17,500.00	
Other Costs (5025 August 31)	$10,265.40	
	$42,589.40	$42,589.40
Sampling		
S.W. Region	$30,000 (Est.)	
W.C. Region	$ 8,500	
Central Region	$ 9,840	
Southeast Region	$ 8,000	
Northeast Region		
Plant Assessments	$12,500	
	$59,000	$59,000.00
Analyses		
MOE (Alachlor - May 5 to Aug. 30)	$64,300	
MOE General CHEM	$66,000	
Regular Pesticide Scans (9 plants)	$28,000	
Special Pesticides (4 plants)	$19,000	
Data Processing	$ 3,000	
OMAF Lab Alachlor	$91,926	
	$272,226	$272,226.00
Alternate Water		
Bottled Water)		
Trucked Water)	$1,000.00	$1,000.00
Drilled Well Equip.	$8,014.89	$ 8,014.89
	TOTAL	$467,061.29

* Powdered Activated & Granular Activated Carbon.

7. ALACHLOR IN FOOD

The metabolism of alachlor in plants is generally understood and the residue data indicate that alachlor is absorbed by corn, peanut and soybean plants from treated soil and the residue appears to be translocated throughout the entire plant. In light of the limits of present methods of analysis for significant levels of alachlor metabolites, the actual measured residue levels and/or the tolerances established to limit the maximum residue level may be lower than appropriate.

The metabolism of alachlor in domestic animals is currently not well understood and the levels of residue of concern in animals and animal products cannot be fully ascertained. Animal feeding studies using both ruminants and poultry have been required by the United States Environmental Protection Agency as a condition for any period of continued registration and were expected to be completed by the fall of 1984.

In the course of the 1985 Drinking Water Monitoring Program, the following produce samples were analyzed for alachlor by the O.M.A.F. laboratory:

a) three samples of corn, two of soybeans, and one of white beans all grown in soil treated with alachlor at planting time.

b) nine samples of canned asparagus and one sample of tomato juice which were processed using water from the Dresden municipal supply.

c) porcine tissue from a farm where swine were drinking water containing in excess of 5 ppb alachlor; tissue samples consisted of 63 muscle tissues from 63 individual animals plus 6 liver and 6 kidney samples taken at random from the same 63 animals.

d) one sample of hen eggs and one sample of human breast milk where well water contained in excess of 5 ug/L alachlor.

All of the above samples contained non-detectable levels of alachlor <0.01 mg/Kg dry weight (<0.01 ppm).

Alachlor recovery studies (spiked samples) were carried out with each of the substrates analyzed and were greater than 75% in all cases.

Under the Food and Drug Act and Regulation, a negligible level of 0.1 mg/Kg (0.1 ppm) of any agricultural chemical or its derevatives is accepted as the guidelines where specific tolerances have not been established and accordingly a negligible level of 0.1 mg/Kg (0.1 ppm) or less for alachlor in corn, potatoes, and soybeans can be used as a guideline. The non-detectable level of 0.01 mg/Kg (0.01 ppm) in the above tested commodities is therefore well below the accepted Canadian guideline.

8. INDEPENDENT REVIEW OF ALACHLOR PROGRAM - M.M. DILLON & ASSOCIATES

Summary

M.M. Dillon Ltd. was retained by the Ontario Ministry of the Environment (MOE) to independently review its alachlor programme for 1985. The review was to assess the suitability of the programme to:

- o accurately identify the incidence of contamination;
- o implement effective short term remediation measures;
- o assess the methodology used to develop the scientific basis for the conclusions reached and the actions taken.

In order to carry out this assessment, the background literature was reviewed to develop an up-to-date position on the use, fate, environmental hazard and analysis of alachlor. With this background knowledge, a series of interviews were conducted with MOE regional staff, laboratory staff at MOE Resources Road and the Ontario Ministry of Agriculture and Food (OMAF) Laboratory in Guelph. The

report is based on data supplied by these staff members and our literature and technical review.

The monitoring programme was found to be located appropriately both on a regional basis for municipal systems and on a local agricultural basis for private wells. Municipal systems were sampled after rainfall events when it was logical to expect the greatest potential surface water contamination from agricultural run-off. Originally private wells were selected for sampling such that any contamination found would be attributable solely to groundwater contamination. This was accomplished by examining the well and its surrounding physical setting; poorly constructed wells, wells in a poor state of repair or wells subject to surface water infiltration were not included in the original sample set. However, as the programme became better known, other wells were included in the sampling probably as a result of individual concerns and local requests to assess a water supply. The data obtained by the MOE clearly identifies these two different situations. In this way the MOE could associate causes of well water contamination with groundwater contamination from the normal use of alachlor or with contamination from poor construction, maintenance or unsafe handling of the alachlor.

Sample taking, handling and transmittal to the laboratories was found to be appropriate in most regards. Some initial problems concerning sampling locations were resolved to the credit of the follow-up procedures MOE had in place to investigate contamination incidents. Field-handled blanks and replicates could have been used to complement the work done to demonstrate the stability of alachlor during the sample and analysis programme.

Analytical methodologies used were similar to those in the published literature. Slight differences were attributable to normal variance in methodologies found in laboratories practicing trace organic analysis. The ability of these labs to detect and quantitate alachlor in water appears to be at the state-of-the-art. Modern quality assurance and quality control procedures are well established at the MOE laboratory although their strict

applicability to trace organic analysis is limited by the nature of trace organic analysis. OMAF labs tend to rely more on their considerable experiences in residue analysis to provide quality assurance; there is some doubt this approach to quality assurance can be relied upon in the critical way data are compared in today's scientific community.

A brief review of the toxicological literature without a critical review of the detail suggests that the action levels for alachlor are appropriate.

The response to contamination events for municipal systems was the application of powdered activated carbon (PAC) to settled drinking water and resampling of raw and treated water throughout the contamination episode. PAC appears to be effective although we would recommend it be added before the clarifier to assist in wetting and mixing of the carbon. Other operation problems like carbon fines and unsightly "creep" marks would be avoided as well.

For private well contamination events, the resupply of drinking water was apparently effectively undertaken for those events identified to us.

Assuming the resupply of water was undertaken consistently, it appears an effective campaign of groundwater protection was undertaken for 1985. A problem of different dimensions exists where contamination can be traced to unsafe practices on well construction. We are concerned that the agricultural community may not be taking suitable precautions to guard against contamination through pathways other than through the ground water.

APPENDIX A

ALACHLOR

Alachlor is the common name for 2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide, CAS number 15972-60-8, a pre-emergent herbicide. It is marketed under the Tradename Lasso^R. The physical and chemical properties of alachlor are:

Empirical Formula	$C_{14}H_{20}NO_2Cl$
Molecular Weight	269.77
Melting Point	40 - 41°C
Specific Gravity	1.133 (25/15.6°C)
Solubility	Soluble in ether, benzene acetone, benzene, ethanol, ethyl acetate; slightly soluble in hexane; solubility in water at 25°C: 242 ppm
Octanol/Water Partition	434
Stability	Stable
Appearance at room temp.	White, crystalline solid at 23°C
Formulations	43.5 and 45.1 emulsifiable concentrates; 10 - 15% granular; microencapsulated.

The biological properties of alachlor are:

Soil partition coefficient, K_d	0.6 - 8.1; most values less than 4.0
Half-life in soil	Approx. 3 weeks depending on soil type and climatic conditions
Foliar absorption characteristics	Absorbed mainly by germinating plant shoots, secondarily by roots
Translocation characteristics	Throughout the plant, with higher concentrations in vegetative parts than in reproductive parts
Adsorption and leaching characteristics in basis soil type	Adsorbed by soil colloids
*Breakdown	Microbial breakdown is main method of degredation
Loss for photodecomposition or volatilization	Low

* Although alachlor is biologically degraded in soil, it does not readily degrade once it reaches an aquatic system.[3]

REFERENCES

1) Herbicide Handbook of the Weed Science Society of America.

2) The Merck Index.

3) Alachlor position document I - EPA, U.S.A. Dec. 1984

APPENDIX B

STABILITY STUDY FOR TRANSIT OF SAMPLES

An experiment was conducted to determine the stability of alachlor over time in tap water under conditions similar to or more extreme than expected during the 1985 Alachlor Field Sampling Program.

The following conditions were investigated:

i) clear glass containers vs. amber
ii) degradation over 192 hrs of storage at 25^{o}C
iii) exposure to sunlight/fluorescent light

Experimental:

A fresh solution of alachlor in tap water was prepared as follows:

(1) 11.317 mg alachlor dissolved in 1L tap water, stirring for 30 minutes (conc = 11.317 mg/L or 11.317 ug/ml).

(2) 8 mls of the above solution were used to spike 16L of tap water, stirring for 1 hour (conc = 5.658 ug/L).

(3) 8 x 800 ml samples were prepared in amber bottles and 8 x 800 ml samples in clear bottles.

(4) Duplicates were extracted within 1 hour of preparation (T_o) and the rest of the samples were stored under normal lab benchtop conditions for periods of 48 hours, 96 hours, and 192 hours. The nominal lab temperature is 25^{o}C and the samples were exposed to fluorescent and sunlight for at least 12 hours each day.

Results:

Average recoveries were calculated with respect to concentration at time zero for samples stored at 25^{o}C.

	48	96	192
Time (hrs)	48	96	192
Average % recovery:			
(i) Amber bottles	112	89	89
(ii) Clear bottles	89	94	95

Conclusions:

There is statistically no significant change in alachlor concentration over time at 25^{o}C (0-192 hrs), after exposure to sunlight/fluorescent light.

APPENDIX C

SAMPLE SUBMISSION PROTOCOL - ALACHLOR STUDY

A sample submission protocol was developed for the alachlor in Drinking Water survey which was done for the 1985 season. The following points were established.

1) Any high priority submission from the Regions requesting alachlor analysis (LIS test name POLASS) will be received as high priority without any further documentation, please use special preauthorized submission forms.

2) The laboratory performing the analysis will be operating on a 7:00 a.m. to 5:00 p.m. schedule. If samples were being collected/shipped during that time period, Regional staff must call 248-3939 (David Hall, Rosalind Cairncross or Patrick Crozier) informing the lab that samples will be forthcoming. If sampling/shipping occurs between 5:00 p.m. and 7:00 a.m. then the call should be made after 7:00 a.m. the next working day.

3) No samples will be accepted unless accompanied by completed LIS submission sheets. This is the only sample tracking system the laboratory will use, therefore inquiries regarding sample status will not be possible without complete information. The Region should keep copies of all LIS submission information.

4) Results will be phoned in to G. Missingham, Water Resources Branch, as soon as the analysis is complete. A final LIS report will follow.

5) The laboratory capacity is 36 samples/day and a 30 hour turn-around time will be offered on those samples. Any samples in addition to the 36 arriving on any one day will cause backlogs and adversely affect turn-around times.

6) The laboratory routine will start at 7:00 a.m. and samples should arrive at the laboratory prior to that time to be run that day. Regular samples arriving after 10:00 a.m. will be run the following day, and after 10:00 a.m. Friday will be run on Monday. Exceptions will be made for "event sampling" after a rain. Staff will be on call through the weekend and such samples will be analysed on the same basis as regular samples i.e. staff will work 7:00 a.m. - 5:00 p.m. as required.

   No other triazine herbicides will be done for these samples. If other triazines are to be analysed a separate bottle and submission sheet is required and 30 hour turnaround will not be available.

APPENDIX D

THE DETAILS OF MOE ANALYTICAL METHOD

Alachlor is a pre-emergent herbicide widely used on corn and soybean crops in Ontario. It is a member of the nitrogen containing herbicides. It is also relatively soluble in water and so finds it way into surface and ground waters via agricultural run-off. Since alachlor is apparently resistent to degradation in water, levels present in these waters are expected to persist unless diluted. Evidence suggests that alachlor is oncogenic (tumor-causing) in laboratory animals.

This methodology was developed to provide a high sample throughput as well as a fast sample turnaround.

Analytical results were required 30 hours after arrival of samples in the lab. A second methodology is available for alachlor as one component of the Triazine analysis.

Sample Handling and Preservation

Samples are to be collected in one litre amber or clear glass bottles with Teflon or aluminium foil lined caps. These bottles are to be labelled "POLASS". Although amber bottles, which are pre-cleaned at the laboratory and shipped to the user, are preferred, our tests have shown that the analysis is not compromised by the use of clear glass bottles as received from the manufacturer.

The minimum sample size required is 800 ml. Samples are adjusted to this volume prior to analysis.

Samples may be stored at room temperature and no special precautions are necessary to protect them from exposure to light.

Caution: Although tests indicate that samples do not require special storage, reasonable precautions ought to be taken against exposure to extremes of temperature, light etc.

Selection of Method for Analysis

The need for a 30 hour turnaround time placed a number of constraints on the choice of an analytical method.

For the gas chromatographic analysis a highly selective detector (nitrogen-phosphorus detector) was chosen. This eliminated the need for removal of organic interferences by column chromatography. A dual column gas chromatographic method provided a high level of assurance of the correct identification of the compound.

All positive results were subjected to analysis by mass spectroscopy for confirmation.

ALACHLOR ANALYSIS - METHOD

SUMMARY

MATRIX: Surface water, treated water, well water.

Interpretation:	Results are reported as ug/L (ppb). Since alachlor is relatively soluble in water, greater concentrations are expected to enter the surface water from the run-off during rain events in the areas where application occurred.
Principle of Method:	The sample is solvent extracted, water is removed from the extract and it is concentrated. The concentrated extract is examined by gas chromatography using a nitrogen-phosphorus detector and external standard quantitation procedure, based on peak areas.
Through-put Capacity:	A maximum of 36 samples per day may be analysed under optimum conditions. A verbal report is available within 30 hours of receipt of the sample.
Range of Application:	1.0 to 20 ug/L alachlor in water. Higher concentrations are diluted and rerun when necessary.
Standard Deviation:	The standard deviation for replicates spiked into tap water at the 1.0 ug/L level is 0.1 ug/L.

Reporting Procedure: The lower reporting limit is 1.0 (ug/L). Values between 0.5 and 1.0 are reported verbally as traces and values >1.0 are reported to the nearest 0.1. To establish the confidence limits of this method, a set of spikes at 1.0 ug/L in tap water was analysed and the standard deviation calculated:

This indicates that a sample containing 1.0 ug/L would give a result of 1.0 $\pm$ 0.2 95% of the time.

Method Detection Limit: In order to establish the method detection limit (MDL), a set of replicates at 0.5 ug/L was analysed and the standard deviation, "s", calculated. In this case, "s" was equal to 0.05 ug/L. According to the recommendations of the ACS, the MDL = 10s i.e. 10 x 0.05 ug/L so the method detection limit is 0.5 ug/L.

Interferences and Shortcomings: While interferences are possible with any method, the risk is obviously greater when the clean-up stage is omitted and the GC runs are short. Dual column GC reduces this risk but cannot eliminate it. All positive samples are therefore examined by mass spectrometry to confirm their identity.

Minimum Volume of Sample: 800 ml. Samples which contain more than 800 mls are adjusted to this level.

Preservation and Sample Container:	One litre pre-cleaned amber glass bottles are acceptable. Caps are to be Teflon or foil lined. No special preservation is needed for the purposes of this program but extremes of temperature, light etc., should be avoided.
Safety Considerations:	The solvents used pose a fire and exposure hazard. The extraction procedures and other steps involving solvents should therefore take place in a fumehood.

ALACHLOR ANALYSIS - METHOD

DETAILS

Introduction

Alachlor is extracted from the water matrix using dichloromethane. The extract is evaporated to dryness and reconstituted to 2 ml in isopropanol. The extract is examined by dual column gas chromatography with nitrogen-phosphorus detectors. Confirmations are done by mass spectroscopy.

Interferences and Shortcomings

Interferences may be possible with this method as with other trace organic analysis. Consequently all glassware is throughly cleaned and rinsed by a procedure including acetone washing, detergent washing, rinsing in tap water followed by distilled water prior to overnight baking at 300°C. In addition blanks are processed with each sample set to verify that contamination has not occurred.

APPARATUS

1. Pipette, Mohr type, transfer 25 ml.
2. Cork rings, 60 mm ID.
3. Phase separating paper, silicone treated, 15 cm.
4. Rotary end-over-end tumbler, 40-60 rpm.
5. Rotary flash evaporator.
6. Filter funnels, 65 mm.
7. Flask, 250 ml, round bottom.
8. Auto sampler vials, Varian, caps and teflon lined septa.
9. Pasteur pipettes
10. Dispensers (0-200 ml), micro dispenser (0-2.5 ml).
11. Graduated cylinder 10 ml.

Gas chromatograph, Varian 3700 with Vista 402 data system or equivalent.

COLUMNS: DB1701, 30 m x 0.25 mm, 0.25 u.
DBWAZ, 30 m x 0.25 mm, 0.25 u.

NOTE: Improvements in technique or procedure are frequently incorporated into the method. The impact of such changes is thoroughly documented before changes are approved. The current conditions may be obtained from the lab.

REAGENTS:

1. Dichloromethane, distilled in glass.
2. Isooctane, distilled in glass.
3. Isopropanol, distilled in glass.
4. Analytical alachlor - 99.5% Monsanto.

GC ANALYSIS

Carrier:	Nitrogen, 2 ml/min
Make-up:	Nitrogen, 30 ml/min
Detector:	Hydrogen, 4.5 ml/min
	Air, 128 ml/min
Injector Temp:	$250^{o}C$
Detector Temp:	$300^{o}C$
Program:	$100^{o}C$ to $230^{o}C$ at $20^{o}C$/min

STOCK SOLUTIONS AND STANDARDS

1. Stock Solution, 100 ug/ml for Standards - Dissolve 0.01 grams of alachlor in isopropanol and make up to 100 ml in a volumatric flask. Standards are prepared by diluting the stock solution to 1 ug/ml.

2. Stock Solutions for Spikes - Dissolve 0.20 grams of alachlor in tap water. A dilution to 0.8 ug/ml is prepared and a 1 ml of this solution is used to spike 800 ml of tap water.

PROCEDURE

NOTE: All glassware and the phase-separating paper is pre-rinsed with dichloromethane for each batch of samples. The combined rinsings are then treated like a sample extract.

1. The sample is vigorously shaken and the volume adjusted to 800 ml by decanting the excess sample.

2. (i) Add 50 ml of dichloromethane to the 1 litre bottle.

   (ii) Place bottle in rotary tumbler and tumble for five (5) minutes. Set up round bottom flasks on cork rings. Place funnels containing phase separating paper on round bottom flasks.

   (iii) Remove bottle from tumbler, allow phases to separate and siphone off lower dichloromethane layer using 25 ml pipette and suction.

   (vi) Transfer extract to funnel holding pre-rinsed phase separating paper.

   (v) Add one more 50 ml aliquot of dichloromethane to sample bottle and repeat steps (ii), (iii) and (iv).

   (vi) Rinse phase separating paper and remove paper and funnel.

   (vii) Add 2 ml of isooctane to extract to act as a keeper.

   (viii) Set up round bottom flask on rotary evaporator and concentrate to approximately 1 ml. (Temperature $30^{o}C$, approximately 35 mm Hg vacuum on water aspirator).

(ix) Add 5 ml of isooctane to sample in round bottom flask and rotary evaporate to dryness.

(x) Add an accurately measured volume of 2 ml isopropanol to round bottom flask taking care to cover all surfaces of the flask using a pasteur pipette.

(xi) Fill a sample vial to approximately 1.5 ml level leaving sufficient head space to allow the autosampler to pressurize the vial.

GAS CHROMATOGRAPHY ANALYSIS

Varian model 3700 or 6000 gas chromatographs fitted with nitrogen-phosphorus detectors are used. These are interfaced to Vista 401 or 402 data systems and compatible printer-plotters. An external standard quantitations method is used based on electronic intergration of peak areas.

CALCULATIONS

The calculations of the amount of alachlor in a sample is based on the following formulae:

<u>For Calibration</u>:

Calibration Factor for Compound 1:

Basic Formula: $CF_1 = \dfrac{\text{Amount}_1}{\text{Area}_1}$

For Quantitation:

Basic Formula: $Amount_1 = Area_1 \times CF_1$

The result is multiplied by the appropriate factor to compensate for dilution (final volume of sample is 2 ml) and for the fact that 800 ml are used instead of one (1) litre (multiplier factor = 2.5).

NOTE: The Vista 401 uses a modified from the above equations to perform the calculations.

MASS SPECTROMETRTY ANALYSIS

A Hewlett-Packard MSD or Finnigan 4500 are used to confirm the identity of the compound when the Gas Chromatography results indicate that alachlor is present.

The analysis is performed in selected ion monitoring mode using the 160, 188, 237 ions and the appropriate area ratios between them.

QUALITY CONTROL AND ASSURANCE

1. In-run QC: Each set of samples (i.e. a 'run') is accompanied by a blank, a spike and a glassware rinse. The workload for the day normally constitutes a run and may vary between 10 and 36 samples.

(i) Blanks: tap water is used as a blank and it is treated exactly as if it were a sample.

This is a glassware/reagent blank that monitors the quality of the procedure and reagents used.

(ii) Spikes: a known amount of alachlor is added to tap water and this is treated exactly as if it were a sample. The spike level for the alachlor program was 1.0 ug/L.

The stock solution used for spiking was prepared in tap water rather than solvent to ensure that the spike resembled a sample as closely as possible.

(iii) Glass/phase separating paper rinse.

The condition of the glassware and the phase separating paper is monitored by pooling the individual dichloromethane, rinsings and treating this as if it were an extract.

GC QA/QC: The calibration of the GC is checked at least once per day.

The first injection and every 10th injection thereafter is a standard.

Adjustments are made for sensitivity changes in the detector. The linearity of the detectors was verified by the injection of replicate standards at each of the following concentrations: 0.5, 1.0, 10.0, 20, 40 ug/L.

The repeatability of injections was determined by replicate injections of a 1.0 ug/L standard.

Method QA/QC: Replicate spikes in tap water at 0.5, 1.0, 5.0, and 20 ug/L were analysed to determine the method linearity and recovery.

Sets of 1 ug/L spikes were analysed to monitor the quality of the extraction procedure with time.

Calculation: Results are reported to the nearest 0.1 ug/L or 2 significant figures.

The lower reporting limit is 1 ug/L. Between 0.5 ug/L and 1.0 ug/L results are verbally reported as traces to the field co-ordinator.

APPENDIX E

Chromatographic conditions

Split-Sample Comparison

LABORATORY	COLUMN TYPE	CARRIER GAS	TEMPERATURE PROGRAM	DETECTOR
MOE chnl 1	CAPILLARY DB1701 30 m x 0.25 mm ID 0.25um stat. phase	Nitrogen 2 ml/min	100 to 230 deg. C 20 deg/min	Nitrogen-Phosphorus
MOE chnl 2	CAPILLARY DBWAX 30 m x 0.25 mm ID 0.25um stat. phase	Nitrogen 2 ml/min	as per chnl 1	Nitrogen-Phosphorus
OMAF chnl 1	CAPILLARY SPB-5 15 m x 0.25 mm ID 0.25um stat. phase	Helium 2 ml/min	60 to 150 deg. C at 20 deg/min to 250 deg. final at 5 deg/min	Nitrogen-Phosphorus
OMAF backup	PACKED 5% Dexil300 on ChromasorbW-HP 1.8 m x 2 mm ID	Helium 50 ml/min	Isothermal at 200 deg. C	Conductivity detector in halogen-specific mode
HC Chnl 1	CAPILLARY DB-5 with SE54 30 m x 0.32 mm	Helium	hold @ 190 deg. for 2 min 2 deg/min to 230 hold 15 min	Nitrogen-Phosphorus
HC Chnl 2	CAPILLARY CARBOWAX 20 m 30 m x 0.25 mm	Helium	as per chnl 1	Nitrogen-Phosphorus
AG.CAN	PACKED 6 ft x 0.25 in ID 1.5% Sp 2250 and 1.95% Sp 2401 on 100/120 Supelcoport	Helium	4 min @ 180 deg. 2 deg/min 2 min @ 200 deg	AFID

APPENDIX F

List of Pesticides Scanned with Detection Limits by the MOE Lab

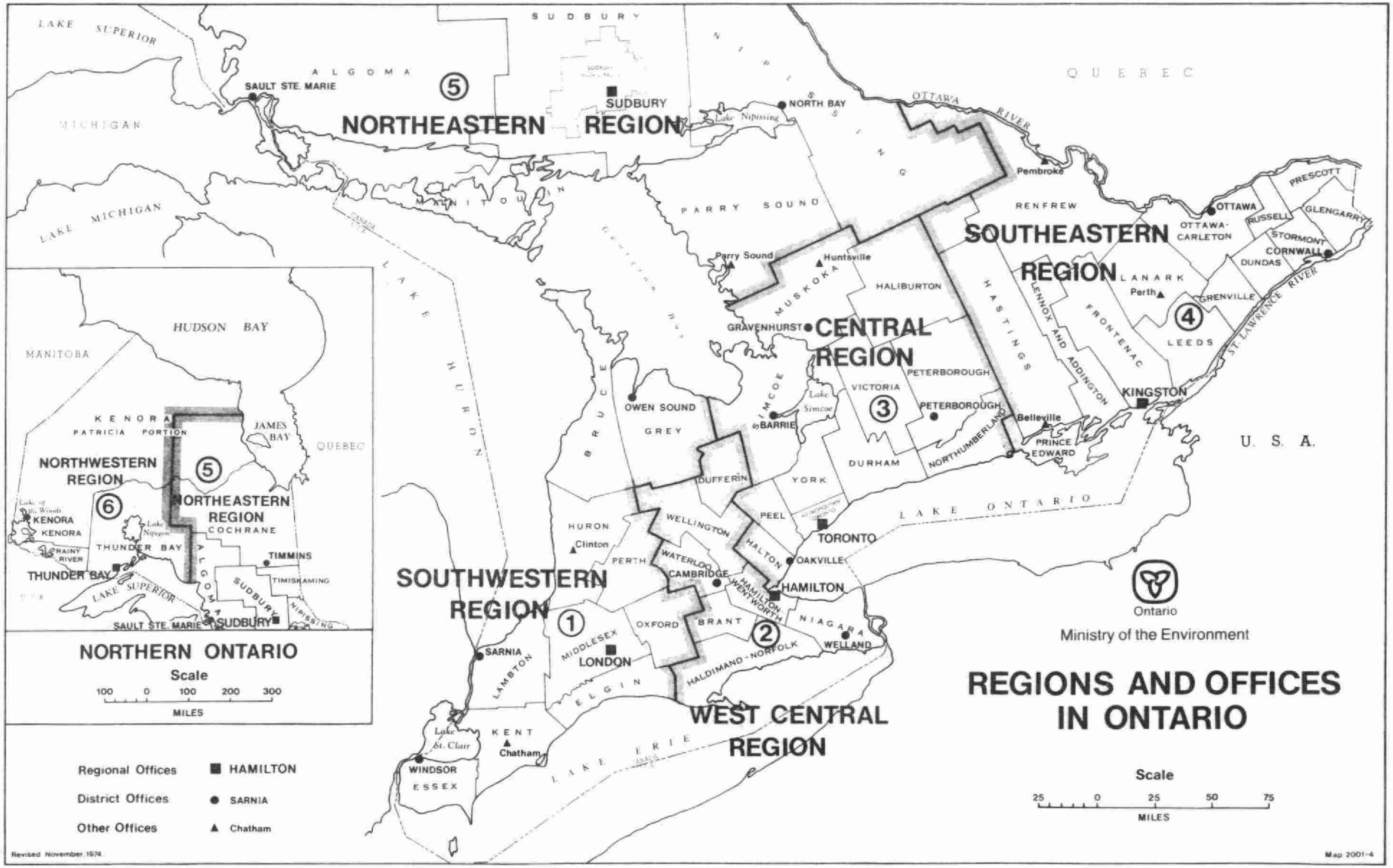
(weekly at Cayuga, Dresden, Harrow and Paisley and monthly at these four plus Alvinston, Amherstburg, Port Stanley, Stoney Point and Wallaceburg)

Pesticide	Detection Limit ng/L
Dicamba	100
2,4-D-Propionic acid	100
2,4-Dichlorophenoxyacetic Acid	100
Silvex	50
2,4,5-Trichlorophenoxyacetic Acid	50
2,4-Dichlorophenoxybutyric Acid	200
Picloram	100
Hexachlorobenzene	1
Heptachlor	1
Aldrin	1
pp-DDE	1
Mirex	5
α-BHC Hexachlorocyclohexane	1
β-BHC Hexachlorocyclohexane	1
γ-BHC Hexachlorocyclohexane	1
α-Chlordane	2
γ-Chlordane	2
Oxychlordane	2
op-DDT	5
pp-DDD	5
pp-DDT	5
DMDT Methoxychlor	5
Heptachlorepoxide	1
Endosulfan I	2
Dieldrin	2
Endrin	4
Endosulfan II	4
Endosulfan Sulphate	4
Ametrine	50
Atrazine	50
Cyanazine	100
Prometone	50
Propazine	50
Prometryne	50
Metribuzin	100
Simazine	50

NOTE: Analytical methods for pesticides available if requested.

APPENDIX G

Ontario Counties and MOE Regions



APPENDIX H

Data on Positive Private Wells
(as of December 3, 1985)

Southwestern Region

1. Well No. SW 107

Sampling Period - May 31 to November 13

Sample Results ug/L (approx. weekly intervals):

ND, ND, ND, 1.0, ND, ND, ND, ND, ND, ND, ND, ND, ND
(ND = Not Detected)

Remarks:
- dug well, 20' deep;
- estimated over 100 year old;
- walls - field - stone cribbing;
- soil - loam;
- 50' from corn and soybean fields;
- drainage away from well;
- well used for drinking is a sand point 50' from old well, negative for alachlor.

Conclusion: contamination probably due to poor construction and overland surface contamination.

2. Well No. SW 110

Sampling Period - June 18 to November 13

Sample Results ug/L (approx. weekly intervals):

T, 1.1, ND, T, ND, ND, ND, ND*, ND*, ND, ND*, 1.1*, ND*, ND, ND, ND, ND, ND (T = Trace Result) (* indicates background chemical data available)

Remarks:
- dug well, 17' deep;
- brick lined, 6' diam;
- poured concrete top, opening 10" above ground;
- seepage running down inside brick wall;
- susceptible to spills near well, no evidence of any spills;
- chemical odour noted in well;
- nearest field 60';
- corn field 80' away, separated from by large ditch and driveway;
- alachlor and atrizine used;
- soil clay-loam;
- in samples with *, nitrate and potassium <0.01 to 1.45 and 0.5 to 0.9 mg/L respectively;
- very low probability of overland contamination of well;
- owner has been using bottled water for drinking for 5 years.

Conclusion: alachlor in well probably due to ground water contamination.

3. Well No. SW 125

Sampling Period - May 28 to November 13

Sample Results ug/L (approx. weekly intervals):

55, 39, 40, ND, 1.3, ND, 25, T, ND, ND, T, ND, ND, ND, ND*, ND, ND*, ND, ND, ND

Remarks:
- dug well, 20' to 25' deep;
- brick lined;
- closest field is 150' away;
- soil type is sand;
- samples with * had nitrate and potassium levels <0.01 to 0.03 and 0.5 to 1.4 mg/L respectively;
- spring of 1985, a spill of alachlor spray mixture near well;
- water supplied - May to mid-July from Colchester plant.

Conclusion: alachlor contamination due to spill in vicinity of well.

4. Well No. SW 140

Sampling Period - May 28 to November 13

Sample Results ug/L (approx. weekly intervals):

3.9, T, T, ND, ND, ND, ND, ND, ND, ND, ND*, ND*, ND*, 12*, ND*, ND*, ND, ND, ND, ND, ND, ND

Remarks:
- dug well, 50' deep;
- originally a stone lined dug well 25' deep;
- in an effort to upgrade put 3' diam. well tiles inside old well, leaving 1' open space between old and new walls;
- top is 3 imperfectly laid slabs flush with soil surface;
- soil is very light sand;
- corn fields 20' and 100' away, in heavy rain runoff from both fields could pass over well area, alachlor used;
- samples with * had elevated nitrate and potassium levels of 7.3 to 12.2 and 8.7 to 10.8 mg/L respectively;
- high probability of overland surface contamination;
- well is used for drinking by family with no control over chemical usage in fields;
- alternate water supplied.

Conclusion: contamination of well probably due to overland runoff from corn fields.

Southwestern Region (continued)

5. Well No. SW 142

Sampling Period - May 28 to November 13

Sample Results ug/L (approx. weekly intervals):

2.7, T, 1.7, ND, ND, ND, ND, ND, ND, ND, ND, ND*, ND*, ND*, ND*, ND*, ND*, ND, ND, ND, ND, ND

Remarks:
- sand point, 15' deep, below basement floor of 3 year old house;
- well to current engineering standard;
- no physical contact of well head and ground surface;
- nearest corn field 100', alachlor used;
- sandy soil;
- during high rainfall drainage tile around house may be gateway for alachlor laden waters to well;
- samples with * had high nitrate and low potassium (46.5 to 55 and 0.45 to 0.65 mg/L respectively;
- a rural residnetial property;
- well is used for drinking but owner has no control over chemicals used on fields;
- low probability of overland surface contamination.

Conclusion: alachlor in well probably due to ground water contamination.

6. Well No. SW 148

Sampling Period - May 28 to November 13

Sample Results ug/L (approx. weekly intervals):

1.4, 5.6, 18.0, ND, 1.0, 1.1, 1.1, ND, ND, T, ND, ND, ND, ND*, ND*, ND*, ND*, ND*, ND*, ND, ND, ND, ND, ND

Remarks:
- two dug wells, 10' apart, 20' deep and interconnected by a plastic hose below ground;
- one well was properly constructed to today's standards, while the second was not grouted but of good construction;
- 3' diam. concrete well tiles, top caps elevated 10-12" above corn field but below existing road grade;
- corn field owned by another person, 10-12' from well;
- soil - sand;
- wells subject to flooding during heavy rainfall;
- samples with * had nitrate and potassium levels of 1.3 to 1.7 and 1.5 to 2.7 mg/L respectively;
- wells used for drinking, bottled water supplied when alachlor exceeded 5 ug/L;
- wells cone of influence extends under corn field, during heavy draw contaminated water may be drawn into well;
- overland surface contamination possible.

Conclusion: high level contamination (2nd and 3rd samples) probably from overland runoff but numerous low level results may be due to ground water contamination.

Southwestern Region (continued)

7. Well No. SW 149

Sampling Period - May 28 to November 13

Sample Results ug/L (approx. weekly intervals):

ND, ND, ND, 6.6, ND, T, T, ND, 7.7, ND, ND, ND, ND*, ND*, ND*, ND*, ND*, ND, ND, ND, ND, ND, ND, ND

Remarks:
- bored well, 80' deep, 3' diam. well tiles and concrete cap;
- elevated above grade and surface water is directed away from the well proper;
- located 10' from corner of pig barn and 20' from corn field;
- corn field belongs to house owner;
- well is upslope from the corn field and would not receive surface runoff even during heavy rainfall;
- well is properly constructed and sited;
- soil is a sand-loam;
- well provides water for both house and pig barn, therefore, subjected to high water usage;
- due to heavy water usage, the cone of influence would extend under corn field and contamination could be drawn into well by ground water flow;
- low probability of overland surface contamination;
- samples with * had nitrate and potassium concentrations of 0.2 to 1.9 and 0.9 to 1.1 mg/L respectively;
- well used for drinking, no alternate water supplied.

Conclusion: alachlor in well probably due to ground water contamination.

8. Well No. SW 156

Sampling Period - June 5 to November 31

Sample Results ug/L (approx. weekly intervals):

4.0, ND, ND, ND, ND, ND, 7.8, 4.3, 7.8, T, ND*, ND, ND*,
ND, ND*, ND, ND*, ND*, ND*, ND, ND

Remarks:
- drilled well, 67' deep, top 25' is steel encased to prevent surface contamination (house well);
- supplies water to three houses;
- a slope down to corn field, 200' away, of 3 to 5%;
- very low probability of overland surface contamination;
- a second drilled well, 128' deep, used only for the barn, located in machine shed, also sealed with 25' steel casing;
- soil is loam;
- samples with * had nitrate and potassium levels of <0.01 to 0.1 and 1.0 to 1.2 mg/L respectively;
- alachlor not used on farm for four years;
- bottled water supplied when level above 5 ug/L, distillation unit also used.

Conclusion: alachlor in house well appears to be from off-site contamination of ground water.

Southwestern Region (continued)

9. Well No. SW 158

Sampling Period - May 28 to November 13

Sample Results ug/L (approx. weekly intervals):

1.1, T, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND*, ND, ND*, ND*, ND, ND

Remarks:
- dug well, 20' deep, concrete cap;
- house well 50' from fields where alachlor used and 50' from pesticide mixing area, water used for drinking;
- two other wells on property, one in pesticide mixing area;
- alachlor spilled in mixing area in past two years, alachlor used in 1985;
- samples with * had nitrate levels of 2.4 to 3.2 mg/L and some elevated potassium levels of 3.1 to 6.7 mg/L.

Conclusion: alachlor in water may be due to overland runoff from field or from spill in mixing area.

10. Well No. SW 161

Sampling Period - June 3 to November 13

Sample Results ug/L (approx. weekly intervals):

T, 6.3, ND, 18, T, ND, ND, ND, ND, ND, ND, ND, ND, ND*, ND*, ND*, ND*, ND*, ND*, ND, ND, ND, ND, ND

Remarks:
- dug well, 20' deep, brick lined, unsealed, serves only the house;
- set flush with soil surface, some surface flow could pass over area;
- alachlor used in owner's corn field 100' away;
- runoff from field could interact with well during heavy rainfall, therefore, a moderate possibility of overland surface contamination;
- contamination could be reduced with a properly constructed and sealed well;
- a second dug well on property next to barn;
- samples with * had nitrate and potassium levels of 0.02 to 0.25 and 2.5 to 4.8 mg/L respectively;
- distilled water used from June 17 to August 1.

Conclusion: a few high levels of alachlor in water probably due to overland contamination of poorly constructed well.

11. Well No. SW 168

Sampling Period - May 31 to November 13

Sample Results ug/L (approx. weekly intervals):

ND, 1.2, ND, 2.8, ND, T, 1.0, ND, ND, ND*, ND*, ND*, 5.5*, ND*, ND, ND, ND, 4.2, ND

Remarks:
- dug well, 37' deep in sandy soil over hardpan area;
- 3' diam. well tiles with concrete cap;
- located downgrade of owner's corn field, 65' away, and would intercept surface runoff;
- also appeared that ground water flow directed to the well from the field;
- soil sand and gravel;
- samples with * had nitrate and potassium levels of 3.6 to 5.9 and 8.4 to 9.6 mg/L respectively;
- good possibility of overland surface contamination of well and problem could be improved by better site and sealing;
- water used for drinking.

Conclusion: intermittent contamination of well water probably due to overland runoff from corn field.

12. Well No. SW 180

Sampling Period - May 28 to November 13

Sample Results ug/L (approx. weekly intervals):

ND, ND, 1.2, T, ND, ND, ND, ND, ND, ND*, ND, ND*, ND*, ND*, ND, ND, ND, ND, ND, ND

Remarks:
- dug well, 20' deep, 3' diam. concrete tiles;
- constructed to current engineering standards;
- subject to surface runoff only during extremely heavy rainfall;
- located 150' from corn field (alachlor used) and separated from this field by township road and 100' of lawn;
- elevation of well same as corn field;
- normal runoff from corn field intercepted by roadside ditches and directed away from well area;
- low probability of overland surface contamination of well from corn field;
- soil sandy;
- samples with * with nitrate and potassium levels of 1.6 to 1.7 and 0.4 to 0.6 mg/L respectively;
- owner of property uses well for drinking water and does not use any pesticides.

Conclusion: alachlor in well probably from ground water contamination.

13. Well No. SW 215

Sampling Period - July 23 to October 26

Sample Results ug/L (approx. weekly intervals):

12*, 6.8*, 4.4*, 2.2, 2.6*, 3.5*, 3.7, 2.3, 7.7

Remarks:
- dug well, 25' deep, brick lined;
- top flush with ground level and partially covered by metal lid with holes;
- soil sand to clay;
- well not subject to any runoff from treated fields;
- spray equipment filled nearby;
- water pumped into well during spring and summer from pond that receives runoff water from nearby fields;
- very high probability of overland surface contamination by the above route;
- samples with * had elevated potassium and ammonia levels of 68.5 to 86.5 and 1.0 to 1.7 mg/L respectively;
- drinking water from rock well 50' deep;
- soil sample collected on property had a high level of alachlor (8.9 ug/g).

Conclusion: alachlor in well due to overland runoff from treated fields via the pond.

14. Well No. SW 248

Sampling Period - July 30 to November 13

Sample Results ug/L (approx. weekly intervals):

1.2, ND*, ND*, ND*, 3.3*, ND, ND, ND, ND

Remarks:
- two shallow (12') sand points, one connected to electric pump and the other to hand pump;
- both wells close to corn field (alachlor used) which is upgrade;
- evidence of water ponding very close to wells;
- soil is a sandy loam;
- very high probability of overland surface contamination;
- samples with * had nitrate and potassium levels of <0.01 to 0.4 and 0.55 to 0.6 mg/L respectively;
- well only used when working at farm.

Conclusion: alachlor in well probably due to overland runoff from treated field ponding in vicinity of well.

15. Well No. SW 264

Initial Water System

Sampling Period - April 4 to September 28

Sample Results ug/L (approx. weekly intervals):

17, 23, 11, ND, >100, T, 30*, 11*, 13*, 17

Remarks:
- drilled well, 110' deep, pumped into dug well which supplied house and barn usage;
- drilled well with rusted out 25' metal casing allowing easy egress of surface water;
- dug well in depressed area which could collect surface runoff;
- soybean field 20' away from both wells and upgrade;
- very high probability of overland surface contamination;
- samples with * had nitrate and potassium levels of <0.01 to 1.09 and 5.05 to 7.25 mg/L respectively;
- numerous chemical spill sites noted around well;
- owner trucking water from Kerwood.

Conclusion: alachlor in well due to contamination with overland runoff from treated field or spill area.

Improved Water System

Sampling Period - August 22 to November 13

Sample Results ug/L (approx. weekly intervals):

4.9*, 4.7, ND*, ND*, ND, ND, ND, ND, ND

Remarks:
- new drilled well, 128' deep, sealed to a depth of 25' with cast iron;
- pumps into poured concrete reservoir with poured concrete cap which is isolated from all surface runoff;
- both the house and the barn supplied via the reservoir;
- water from old well system may have been used to drill new well;
- alachlor not detected when old well system still positive;
- samples with * had nitrate and potassium levels of <0.01 to 0.4 and 5.4 to 7.35 mg/L respectively.

Conclusion: initial alachlor in well probably due to contaminated drilling mud, not detected since.

Data on Positive Private Wells

(as of December 3, 1985)

Central Region

1. Well No. C-005-85

Sampling Period - May 28 to August 13

Sample Results ug/L (approx. weekly intervals):

5.2, 4.1, 5.3, 3.7, 5.4, 6.0, 9.5, 3.5, 9.4, 9.1, 6.3, 15, 12, 12, 9.5

Remarks:
- bored well, 40' deep;
- concrete tile, cap cracked;
- drainage away from well;
- soil - sand and gravel;
- well 75' from corn field used alachlor;
- alachlor mixed off farm;
- bottled water supplied until new well drilled.

Conclusion: alachlor in well due to ground water contamination.

2. Well No. C-N-1

Sampling Period - June 4 to November 14

Sample Results ug/L (approx. weekly intervals):

ND, ND, 2.7, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND

Remarks:
- bored well, 50' deep;
- concrete tiles, joints between and lift holes not sealed;
- well 40' from corn field (alachlor used), drainage from corn field toward well;
- joint inspection Health Unit and MOE, owner advised water fit for consumption subject to further testing, advised to seal joints and lift holes and regrade around well which was done;
- water used for drinking.

Conclusion: alachlor in well due to overland surface contamination and poor well construction.

Central Region (continued)

3. Well No. C-V-6

Sampling Period - June 3 to November 14

Sample Results ug/L (approx. weekly intervals):

T, ND, 1.1, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND

Remarks:
- drilled well, 87' deep;
- located in feed lot;
- general drainage toward well;
- corn field 300' away, alachlor used;
- joint inspection by Health Unit and MOE, owner advised water fit to drink subject to further testing, advised to improve construction - showed little interest;
- water used for drinking.

Conclusion: alachlor in well due to overland runoff from treated field.

Data on Positive Private Wells

(as of December 3, 1985)

Southeastern Region

1. Well No. SE-3

   Sampling Period - June 21 to November 7

   Sample Results ug/L (approx. weekly intervals):

   T, ND, ND, ND, T, 1.3, ND, T, T, T, ND, ND, ND, ND, ND, ND, ND, ND, ND

   Remarks:
   - dug well, 15' deep;
   - abandoned, not used for any purpose;
   - soil 4-5' silty-clay loam over fractured limestone;
   - drainage toward well;
   - 30' from crops, 300' from mixing area;
   - on same property as SE-4.

   Conclusion: alachlor in well probably due to overland surface contamination or through fractured limestone.

Southeastern Region (continued)

2. Well No. SE-4

Sampling Period - June 21 to November 1

Sample Results ug/L (approx. weekly intervals):

ND, 7.5, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND, ND

Remarks:
- drilled well, 45' deep;
- casing is 3.5' down, set in fractured limestone;
- soil 2' silty-clay loam over fractured limestone;
- well 30' from crops, alachlor used;
- drainage toward well;
- limestone outcrop beside field;
- water used for drinking.

Conclusion: alachlor in well water due to overland runoff to well area or through fractured limestone.

3. Well No. RR #1 Winchester

Sampling Period - July 11 to October 1

Sample Results ug/L: 2.7, ND

Remarks:
- dug well;
- contaminated by owner's careless disposal of empty containers;
- no alachlor was detected in the well water used for drinking or bathing.

Conclusion: alachlor in well water due to spill in vicinity of well.

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